



Thermoplastic Composite Material

5 This invention relates to a thermoplastic composite material containing an organic fibrous material or a mixture of two or more organic fibrous materials and a thermoplastic binder. The invention also relates to a process for producing the thermoplastic composite material and to the use of the composite material for coating surfaces of objects and to the objects thus coated. The invention also relates to an adhesive for bonding the composite material to the object to be coated.

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Composite materials are materials which are formed by incorporating a base material, for example in the form of fibers, in a second material (the matrix). Certain properties (for example mechanical properties, surface properties or certain behavior towards external influences) of the incorporated material are utilized for the composite material. The base material may vary widely in its quantity ratio to the matrix surrounding it. Thus, the percentage matrix content of wood-based materials, which include for example the known presspahn boards, is generally only 10 to 15%. By contrast, the percentage matrix content of fiber-reinforced plastics, for example glass fiber-reinforced plastics, can be significantly higher, for example more than 70% or even more than 80%.

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In many cases, it is possible by suitably selecting the base material and the matrix to impart to the composite material certain properties of the base material which are paired with certain properties of the matrix. For example, the use of glass or natural fibers in thermosets can cause the tensile strength of the fibers to be transferred to the plastic matrix which, in turn, contributes further advantages to the composite material in regard to shaping, dimensional stability and processability.

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In many cases, the object of making composite materials is to produce from by-products accumulating in the processing of a certain base material a material which possesses characteristic properties of that base material. The corresponding composite material may then generally be used at least as a substitute for the base material and thus provides for the "substance-related" utilization of the base material waste or by-products. This is the case, for example, with the utilization of wood waste in presspahn

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boards. Another example of the substance-related utilization of waste products is the processing of cutting and stamping waste from the manufacture of leather and shoes to leather fiber materials.

5 Leather waste can be reduced to fibers and can then be processed to leather fiber materials (LEFAs). LEFAs are generally single-layer materials of leather fibers and binders. Even at the end of the thirties, LEFA boards were being used in the shoe industry, for example for the production of counters, insoles and inner soles, slipper soles, heels and welts. LEFA materials were also used to a small extent for industrial
10 leather seals.

Besides such properties as flexibility and durability which qualify leather for use in the shoe industry and in the leather goods industry, leather is being increasingly used in other areas where the decorative features of leather are predominant.
15 However, it has hitherto been difficult or even impossible to use leather as a surface material for furniture fronts, wall and ceiling panels or other consumer goods. In particular, it was particularly difficult to use leather as a surface material for objects with a three-dimensional relief structure.

20 Since leather does not have any thermoplastic properties, it can only be used to a limited extent as a surface coating material. In particular, it is difficult to provide varying three-dimensional relief structures with a smooth leather surface by an economical process.

25 Such economical processes for coating relief-like surfaces of moldings are known, for example, from the film coating industry. In this case, a molding (object) is generally coated with a thermoplastic film by heating the molding and the film to a temperature above the flow transition limit of the plastic film and suitably drawing the film (for example by applying a vacuum between the molding and the plastic film) onto the molding
30 (thermoforming). In general, an adhesive establishes a permanent bond between the plastic film and the molding.

 However, a process such as this, which can be efficiently carried out with machine assistance, requires a thermoplastic film as the coating material. Hitherto,
35 however, it has not been possible to finish leather-like substitute materials, for example

LEFAs, in such a way that, on the one hand, they show the thermoplastic properties which are required for use in thermoforming processes but, on the hand, still have leather-like surface properties.

5 WO 98/50617 relates to a thermoplastic composite material which contains, for example, leather and a binder, the binder containing polyacrylates of at least one aqueous anionic polyacrylate dispersion and at least one aqueous cationic polyacrylate dispersion. The described composite materials have the disadvantage of limited cohesion so that, for example where the described composite materials are used in
10 thermoforming processes, only limited profile depths (radii) can be coated without the composite material tearing.

Accordingly, the problem addressed by the present invention was to provide a composite material which would largely exhibit the properties of the natural fibers used
15 as the base material, but which on the other hand would be suitable for use in modern thermoforming processes by virtue of its thermoplastic properties, would have sufficient cohesion for the crack-free coating and "bridging" of large profile depths and which, in addition, would be easy to produce.

20 Another problem addressed by the present invention was to provide an adhesive with which the thermoplastic composite material could be firmly and durably bonded to a number of surfaces in the course of machine processing.

It has now been found that a thermoplastic composite material containing organic
25 fibers material, more particularly leather fibers, and a thermoplastic binder as the matrix material can be obtained providing the matrix material used is a thermoplastic binder which contains at least 10% by weight of a polymer selected from the group consisting of polyurethanes, polyesters, polyamides, polyolefins, polyvinyl esters, polyethers, polystyrenes, styrene/olefin copolymers, polyacrylates or ethylene/vinyl acetate
30 copolymers or mixtures or copolymers of two or more of the polymers mentioned, the matrix material not consisting solely of two polyacrylates.

The thermoplastic composite material obtainable from the polymers mentioned above preferably has a flow transition limit of about 70 to about 130°C.

Accordingly, the present invention relates to a thermoplastic composite material containing

a) at least 15% by weight of an organic fibrous material or of a mixture of two or more organic fibrous materials as component A and

5 b) at least 15% by weight of a thermoplastic binder as component B,
the binder containing at least 10% by weight of a polymer selected from the group consisting of polyurethanes, polyesters, polyamides, polyolefins, polyvinyl esters, polyethers, polystyrenes, styrene/olefin copolymers, polyacrylates or ethylene/vinyl acetate copolymers or mixtures or copolymers of two or more of the polymers
10 mentioned, the binder not consisting solely of two different polyacrylates.

Component A of the thermoplastic composite material may be any organic fibrous material which provides the thermoplastic composite material with the properties required by the user, for example a certain appearance or a certain feel. Organic fibrous
15 materials in the context of the present invention are understood to be both naturally obtained or naturally obtainable fibers and synthetic fibers providing they have an "organic base". Accordingly, organic fibrous materials do not include, for example, such fibers as asbestos, glass fibers or carbon fibers.

20 In addition, no distinction is made in the present specification between materials which occur naturally in fibrous form and materials which have to be given a fibrous structure by a certain treatment step. In addition, among the natural materials, both vegetable and animal organic fibrous materials are suitable for the purposes of the invention.

25 Synthetic fibers, vegetable fibers or animal fibers are normally used for the purposes of the invention.

Suitable natural fibers include, for example, animal fibers, such as wool, hair or
30 silk. Other suitable natural fibers are vegetable fibers, for example cotton, kapok, flax, hemp, jute, kenaf, ramie, broom, abaca, coconut or sisal. Suitable synthetic fibers of natural polymers are cupro fibers, viscose fibers, modal fibers, acetate fibers, triacetate fibers and protein fibers or alginate fibers or mixtures of two or more of the fibers mentioned.

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Suitable fibers of synthetic polymers are, for example, polyacrylic, polymethacrylic, polyvinyl chloride, fluorine-containing polymer fibers, polyethylene, polypropylene, vinyl acetate, polyacrylonitrile, polyamide, polyester and polyurethane fibers.

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However, it is particularly preferred to use leather fibers as the organic fibrous material. To obtain these fibers, leather waste is fiberized and size-reduced by a suitable process so that the fibers obtained can be subsequently used in the process according to the invention for producing a thermoplastic composite material with leather-like properties.

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Basically, the leather fibers may be obtained from any type of leather waste. The leather waste may originate both from chrome-tanned leather and from vegetable-tanned leather. Leathers suitable for use in accordance with the invention include, for example, box leathers, such as hide box, calf box or mast box, buffed box, glazed kid, suede, kid, sandal leather, sole leather, lining leather, nappa leather, glove leather, buckskin, harness leather and industrial leather, chamois leather, hatband leather or transparent leather.

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Depending on the decorative or mechanical effect required, the organic fibrous material may be size-reduced to a stretched length of about 0.1 to 15 mm. Where leather fibers in particular are used, fiber lengths of about 0.5 to 13 mm are suitable, fiber lengths of about 1 mm to about 10 mm being preferred and fiber lengths of about 3 to about 8 mm particularly preferred. The fiber length is measured in the stretched state of the fibers. Depending on the starting material used and the size reduction method applied, the fibers may of course assume an irregularly curved shape in the absence of any external influence.

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Component A is present as the base material of the thermoplastic composite material according to the invention in a quantity of at least about 10% by weight. The thermoplastic composite material increasingly assumes the properties of the organic fibrous material with increasing percentage content of component A. Accordingly, depending on the desired effect, it can be of advantage to use, for example, at least 20% by weight or at least about 25% by weight of component A in the thermoplastic composite material according to the invention. However, the percentage content of the

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organic fibrous material may even be greater, for example about 30% by weight, 35% by weight, 40% by weight, 45% by weight or even more than about 50% by weight, percentage contents of for example 55% by weight or even 60% by weight and more being possible. In one particularly preferred embodiment, the percentage content of
5 fibrous materials is about 15 to about 50% by weight, percentage contents of about 25 to less than about 45% by weight being most particularly preferred.

Leather fibers are preferably present as component A in the thermoplastic composite material according to the invention.
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In order to provide the thermoplastic composite material with the thermoplastic properties required for further processing, the thermoplastic composite material contains a thermoplastic binder as component B.

15 Binders in the context of the present invention are understood to be polymeric compounds which serve as the matrix of the composite material. Polymeric materials with a molecular weight of more than about 1,000 are generally used as binders. However, the molecular weight is preferably higher.

20 The molecular weight (M_n) of the polymers present in the binder is preferably in the range from about 10,000 to about 1,000,000, more preferably in the range from about 20,000 to about 300,000 and most preferably in the range from about 50,000 to about 150,000.

25 In the context of the present invention, the term "binder" is used for the polymeric matrix material as a whole, irrespective of the number of its constituent polymer components and irrespective of how many different preparations containing the polymers forming the binder were required for its production.

30 The molecular weight distribution of the polymers, which can be determined for example by gel permeation chromatography (GPC), does not have to be monomodal. If desired, the thermoplastic binder may also have a bimodal or higher modal distribution.

35 A binder containing at least 10% by weight of a polymer selected from the

group consisting of polyurethanes, polyesters, polyamides, polyolefins, polyvinyl esters, polyethers, polystyrenes, styrene/olefin copolymers, polyacrylates or ethylene/vinyl acetate copolymers or mixtures or copolymers of two or more of the polymers mentioned, the matrix material not consisting solely of two polyacrylates, is
5 used for the production of the thermoplastic composite material according to the invention.

In a preferred embodiment of the invention, binders containing at least two different polymers are used for the production of the thermoplastic composite materials.
10 "Two different polymers" in the context of the invention are understood to be two polymer types which differ in their chemical composition, i.e. in the nature of the monomers involved in the synthesis of the polymer or - where two or more monomers are involved in the synthesis of the polymer - in the ratio of those monomers to one another or in both. It does not matter whether the individual polymer has thermoplastic
15 properties as long as the mixture of two different polymers has corresponding thermoplasticity.

Polyurethanes in the context of the present invention are understood to be any polymers which contain at least two urethane groups in the polymer backbone.
20 Polyurethanes suitable for the purposes of the present invention are any thermoplastic polyurethanes known to the expert on polyurethane chemistry, more especially polyurethanes of the type normally used in the production of thermoplastic moldings, more particularly films, or for the thermoplastic coating of surfaces. Suitable polyurethanes are, for example, polyester polyurethanes or polyether polyurethanes
25 obtainable by reaction of dicarboxylic acids with corresponding polyhydric alcohols, more especially dihydric alcohols, for example dihydric polyethers, such as polyethylene oxide, to form polyether or polyester polyols and subsequent reaction of the corresponding polyether or polyester polyols with di- or polyfunctional isocyanates.

30 Polyesters in the context of the present invention are any polymers containing at least two ester groups and no urethane groups in the polymer backbone. Polyesters suitable for the purposes of the present invention are any thermoplastic polyesters known to the expert, more especially polyesters of the type normally used in the production of thermoplastic moldings, more particularly films, or for the thermoplastic
35 coating of surfaces. Suitable polyesters are, for example, the polyesters obtainable by

reaction of dicarboxylic acids with corresponding polyhydric alcohols, more especially dihydric alcohols, for example difunctional polyethers, such as polyethylene oxide.

Compounds suitable for the production of corresponding polyurethanes or
5 polyesters are mentioned hereinafter.

Polyamides in the context of the present invention are any thermoplastic polyamides of the type obtainable by reaction of suitable di- or polycarboxylic acids with corresponding amines.
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Polyolefins suitable for the purposes of the present invention are obtainable, for example, by radical or co-ordinative polymerization of α -olefins, more especially ethylene or propylene.

15 Polyvinyl esters suitable for the purposes of the present invention are, in particular, polymers of vinyl acetate.

Polyethers suitable for the purposes of the invention are, for example, polyethylene oxide, polypropylene oxide, polybutylene oxide or polytetrahydrofuran,
20 more particularly with a molecular weight of more than about 5,000.

Suitable polystyrenes are, for example, the polymers of styrene or α -methyl styrene.

25 Other polymers suitable for use in the binder of the thermoplastic composite material according to the invention are the styrene/olefin copolymers obtainable by copolymerization of styrene with mono- or diolefins, more especially butadiene. A preferred embodiment of the invention is characterized by the use of the styrene/butadiene copolymers obtainable, for example, under the name of Kagetex
30 LBS 3565 or Kagetex LBS 3060 from Kautschukgesellschaft or under the name of Intex 131 from Enichem or under the name of 28 W 20 from Synthomerchemie.

Suitable polyvinyl esters are the polymers of the esters of unsaturated alcohols with corresponding carboxylic acids. Suitable unsaturated alcohols are, for example,
35 unsaturated aliphatic alcohols containing 2 to about 22 carbon atoms, more especially 2

to about 8 carbon atoms. Suitable carboxylic acids are linear and branched alkanolic acids containing 2 to about 22 carbon atoms, more especially 2 to about 8 carbon atoms. A preferred embodiment of the invention is characterized by the use of polyvinyl acetate. Suitable polyvinyl acetates are obtainable, for example, under the name of
5 Vinnapas D50 from Wacker, Mowilith D 60 from Clariant or Vinnamul 60 044, Vinnamul 9300, Vinnamul 9960 or Vinnamul 84125 from Vinnamul (NL).

Polymers present in the form of an aqueous dispersion are preferably used for the production of the composite materials according to the invention. The dispersions
10 may be anionically stabilized or cationically stabilized polymer dispersions. The dispersion may be stabilized, for example, by self-emulsifiable polymers, i.e. by polymers bearing corresponding hydrophilic groups, for example carboxylic acid groups or amino groups. However, dispersions stabilized by suitable anionic or cationic dispersants or emulsifiers may also be used.

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The terms "polyacrylate" and "polyacrylates" used in the present text apply in the following both to polymers or copolymers of acrylic acid and/or derivatives thereof and to polymers or copolymers of methacrylic acid and/or derivatives thereof.

20 Polyacrylates can be produced by subjecting acrylic acid and/or methacrylic acid and/or derivatives of acrylic acid and/or methacrylic acid, for example esters thereof with monohydric or polyhydric alcohols, either on their own or in the form of mixtures of two or more thereof in known manner to polymerization, for example radical or ionic polymerization. Polyacrylates in the form of an anionic dispersion
25 obtainable, for example, by emulsion polymerization of the corresponding monomers and comonomers are preferred for the purposes of the invention. In general, aqueous anionic dispersions contain, for example, the sodium, potassium and/or ammonium salts of long-chain aliphatic carboxylic acids and/or sulfonic acids for emulsification. However, alkali metal C₁₀₋₁₈ alkyl sulfates, ethoxylated and sulfated and/or sulfonated
30 long-chain aliphatic alcohols or alkylphenols and sulfodicarboxylic acid esters are also suitable.

Homopolymers or copolymers which, besides the acrylates, also contain styrene, acrylonitrile, vinyl acetate, vinyl propionate, vinyl chloride, vinylidene chloride
35 and/or butadiene may be used as polyacrylates in accordance with the present

invention.

Monomers suitable for use in the production of the polyacrylates are, in particular, methyl acrylate, ethyl acrylate, n-butyl acrylate, isobutyl acrylate, tert.butyl
 5 acrylate, hexyl acrylate, 2-ethylhexyl acrylate and lauryl acrylate. Acrylic acid, methacrylic acid, acrylamide or methacrylamide may optionally be added in small quantities as further monomers during the polymerization reaction.

Other acrylates and/or methacrylates containing one or more functional groups
 10 may optionally be present during the polymerization reaction. Examples of these other acrylates and/or methacrylates are maleic acid, itaconic acid, butanediol diacrylate, hexanediol diacrylate, triethylene glycol diacrylate, tetraethylene glycol diacrylate, neopentyl glycol diacrylate, trimethylol propane triacrylate, 2-hydroxyethyl acrylate, 2-
 15 hydroxyethyl methacrylate, hydroxypropyl acrylate, propylene glycol methacrylate, butanediol monoacrylate, ethyl diglycol acrylate and, for example, 2-acrylamido-2-methyl propane sulfonic acid as a monomer containing sulfonic acid groups.

Acrylate/vinyl ester copolymers, acrylate/styrene copolymers and acrylate/methacrylate copolymers are particularly preferred. Polyacrylate dispersions
 20 of the type marketed by BASF AG, Ludwigshafen, under the registered name of Acronal®, more particularly the products Acronal® 500 D and Acronal® S312 D, are particularly preferred and suitable for use in the thermoplastic composite materials according to the invention. In general, anionic polyacrylate dispersions contain only one
 25 type of polymer. If two different polyacrylates from anionic dispersions are to be used, it will generally be necessary to use two different anionic dispersions which contain the particular polymer in dispersed form. According to the invention, however, it is immaterial whether the different polyacrylates preferably present in the matrix are
 30 present in a single dispersion or whether they have been obtained from two or more different dispersions.

In a preferred embodiment of the invention, the binder used as component B contains at least two of the above-mentioned polymers, the total percentage content of the two polymers in the binder as a whole, i.e. in component B as a whole, being at least about 10% by weight, for example at least about 20% by weight, at least about
 35 30% by weight or at least about 40% by weight or more, for example at least about 50

to about 70% by weight or up to about 80% by weight.

In another preferred embodiment of the invention, the binder used as component B contains only one polyacrylate besides two of the above-mentioned polymer types or no polyacrylate.

In another preferred embodiment of the invention, the binder contains at least one polyvinyl acetate and at least one styrene/butadiene copolymer, more particularly a corresponding block copolymer.

It has also been found that the thermoplastic properties of the thermoplastic composite material according to the invention can be influenced by choosing polyacrylates having a suitable minimum film forming temperature. The minimum film forming temperature of a polymer is the lowest temperature at which a dispersion still just forms a coherent film after evaporation of the water. It is close to the glass transition temperature T_g of the polymer and with film formation determines one of the most important performance properties of a polymer dispersion. The minimum film forming temperature (MFT) is generally determined in accordance with DIN 53787. The measuring instrument used is a metal plate to which a temperature gradient is applied. The film is observed for the temperature at which it begins to develop cracks or for the location of the so-called white point at which the cloudy film begins to become clear.

In a preferred embodiment of the invention, at least one of the polymers has an MFT of up to 30°C.

In another preferred embodiment of the invention, at least one of the polymers has an MFT of about up to 5°C and at least one other polymer has an MFT of about 15°C to about 25°C.

Component B as a whole preferably makes up at least about 20% by weight of the thermoplastic composite material. It can be of advantage, for example for selective property modifications, if the thermoplastic composite material contains at least about 30% by weight or at least about 40% by weight or more of component B, for example at least about 50 to at least about 80% by weight. In a preferred embodiment of the invention, component B makes up about 50 to about 75% by weight of the

thermoplastic composite material as a whole.

Besides the organic fibrous material as component A and the thermoplastic binder as component B, the thermoplastic composite material according to the invention may contain other components, preferably in a quantity of up to about 20% by weight. These other components include, for example, inorganic salts, cationic polymers, preservatives, dyes, natural and/or synthetic fats, paraffins, natural and/or synthetic oils, silicone oils and ionic and/or nonionic surfactants.

Salts of aluminum or copper are preferably used as the inorganic salts, aluminum sulfate being particularly preferred.

The inorganic salts are generally used in the production process, which will be described hereinafter, to precipitate (coagulate) the polymeric binder. In general, most of the metal salt is removed from the composite material with the aqueous phase although a small residue can remain in the composite material.

Cationic polymers or cationically charged polymers are polymers which carry positive charges on the polymer backbone or on side groups covalently bonded to the polymer backbone.

Cationic charges can be applied to a polymer by application of suitable cationic groups. "Cationic groups" are understood to be groups which either carry a positive charge or which can be converted into a group carrying a cationic charge by a simple reaction, for example quaternization. In general, the groups in question are amine or ammonium groups.

"Quaternization" is understood to be a reaction in which a primary, secondary or tertiary amine is converted into the tetravalent positively charged form by reaction with a suitable reagent. Suitable reagents are, for example, alkyl halides, more especially alkyl chlorides, alkyl bromides and alkyl iodides, and protonic acids, for example mineral acids, such as hydrohalic acid, phosphoric acid, sulfuric acid, or strong organic acids, such as formic or acetic acid.

Suitably modified polyacrylates, polyesters, polyurethanes or other polymers

carrying at least one primary, secondary or tertiary nitrogen atom may be used as the polymers bearing cationic groups. Polyacrylates bearing cationic groups are preferably used for the purposes of the present invention.

5 Corresponding polyacrylates can be produced, for example, by copolymerizing the monomers described above (except for the monomers bearing free acid groups) together with a suitable ethylenically unsaturated compound bearing a primary, secondary or tertiary amino group. Suitable ethylenically unsaturated monomers containing primary, secondary or tertiary amino groups are, for example,
 10 dimethylaminoethyl methacrylate, dimethylaminoneopentyl acrylate, dimethylaminopropyl methacrylate, aminoethyl methacrylate, 2-N-morpholinoethyl acrylate, tert.butylaminoethyl methyl acrylate, 4-methacrylamido-2,2,6,6-tetramethyl piperidine, trimethyl ammonium methyl (meth)acrylate chloride, α -acetamidodiethyl aminoethyl (meth)acrylate chloride, trimethyl ammonium propyl acrylate chloride or
 15 methacrylate chloride, trimethyl ammonium methyl acrylate bromide or methacrylate bromide, trimethyl ammonium neopentyl methacrylate chloride or acrylate chloride, diallyl dimethyl ammonium chloride, diallyl butyl methyl ammonium bromide. The cationically charged polymers preferably have a pH value of about 3 to about 8 although, in one particularly preferred embodiment, the pH value of the cationically
 20 charged polymers is neutral, i.e. in the range from about 6.5 to about 7.5.

The charge density, i.e. the number of cationic groups per unit weight in the polymer, is preferably about 2 to about 6 meq/g and, in one particularly preferred embodiment, is in the range from about 2.5 to about 5 meq/g. Most particularly preferred charge densities
 25 are in the range from about 3.5 to about 4.5 meq/g.

The cationic polymer generally has a molecular weight of about 1,000 to about 500,000, molecular weights of about 50,000 to about 150,000 being preferred and those in the range from about 80,000 to about 120,000 being particularly preferred.

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Preferred preservatives are those which have a fungicidal action spectrum. The preservative Preventol® A11D marketed by Bayer AG, Leverkusen, is particularly suitable for the purposes of the present invention.

35 In one particularly preferred embodiment, component B contains at least 50%

by weight of polyvinyl acetate.

In another preferred embodiment of the invention, component B contains at least 20% by weight of a copolymer of butadiene and styrene.

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In another preferred embodiment, the thermoplastic composite material contains

- about 10 to about 50% by weight of organic fibers,
- about 10 to about 40% by weight of at least one copolymer of styrene and butadiene,
- about 30 to about 60% by weight of polyvinyl acetate and
- optionally up to 25% by weight of inorganic salts, preservatives, dyes, natural and/or synthetic fats, paraffins, natural and/or synthetic oils, silicone oils, ionic and/or nonionic surfactants.

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The thermoplastic composite material according to the invention is preferably intended for coating surfaces having a relief structure. Such coatings are normally applied by so-called thermoforming. In a preferred embodiment of the invention, the thermoplastic composite material has a flow transition range of about 70 to 130°C.

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At temperatures above the flow transition range mentioned, the thermoplastic composite materials according to the invention can undergo irreversible dimensional changes, for example elongation. By virtue of its particular tear strength coupled with its good flow behavior, the thermoplastic composite material according to the invention is even able to coat reliefs with considerable differences in height (radii) without cracks in the coating and without any change in the original surface structure.

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The thermoplastic composite material according to the invention is preferably produced by contacting component A with the constituents of component B, these constituents preferably being present in the form of an aqueous dispersion.

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If component B contains more than one constituent, i.e. more than one polymer, both polymers may be present alongside one another in one and the same dispersion. However, in another embodiment of the invention, the two polymers may be present in different dispersions.

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In the production process according to the invention, component A and the constituents of component B are mixed in one or more dispersions and the constituents of component B are coagulated simultaneously, i.e. during mixing, or subsequently, i.e. in a separate process step after mixing.

Accordingly, the present invention also relates to a process for the production of a thermoplastic composite material containing

a) at least 15% by weight of an organic fibrous material or of a mixture of two or more organic fibrous materials as component A and

b) at least 15% by weight of a thermoplastic binder as component B,

in which fibers with a stretched fiber length of 0.1 to 15 mm as component A are mixed simultaneously or successively in any order with a polymer dispersion or a mixture of two or more polymer dispersions each containing at least one polymer selected from the group consisting of polyurethanes, polyesters, polyamides, polyolefins, polyvinyl esters, polyethers, polystyrenes, styrene/olefin copolymers, polyacrylates or ethylene/vinyl acetate copolymers or mixtures or copolymers of two or more of the polymers mentioned, the dispersion(s) not consisting solely of two different polyacrylates, to form a mixture so that the polymers present in the dispersion(s) form component B, after which the mixture is treated with an aqueous solution of an aluminum salt or a copper salt, dewatered and dried.

If two or more different polymer dispersions are used, differently stabilized dispersions, for example, may be used in accordance with the invention. For example, where two polymer dispersions are used, an anionically stabilized dispersion and a cationically stabilized dispersion may be used. The dispersions may be selected so that substantially complete coagulation, i.e. substantially complete precipitation of the binders present in the dispersion, occurs. However, the binders may also be only partly precipitated.

However, a preferred embodiment of the invention is characterized by the use of polymer dispersions which are stabilized substantially identically, at least in regard to the charge of the stabilizing species. For example, anionically or cationically stabilized dispersions may be used. In another preferred embodiment of the invention, anionically stabilized polymer dispersions are used.

The treatment of the mixture with an aqueous solution of an aluminum or copper salt is conducted in such a way that, after the treatment, substantially all polymer molecules present in the mixture are precipitated, i.e. coagulated.

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The following exemplary description of the process is merely intended to illustrate one way of carrying out the process according to the invention and does not represent a limitation. Modifications of subsequent process steps, optionally with a view to optimizing the process described hereinafter, may readily be undertaken by the expert according to the situation confronting him.

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To produce the thermoplastic composite materials according to the invention, tanned leather waste is size-reduced (precut) in cutter mills to a size of about 1 cm². At this stage, size reduction is generally carried out under dry conditions.

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The leather waste thus precut is weighed and then wet-fiberized in so-called disk refiners. The addition of water is controlled in such a way that a lump-free fiber slurry consisting of about 5% by weight of fibers and about 95% by weight of water is formed (corresponding to about 1,000 kg of fibers to 20 m³ of water). The size reduction step is preferably carried out in such a way that part of the wastewater subsequently formed in the process is returned to the circuit at this point. In this way, around 50% and preferably more of the water required for the size reduction step is made up of wastewater.

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The suspension of leather fibers in water obtainable in this way is then transferred to a suitable vessel, preferably a mixing vat. The quantity transferred is gauged in such a way that the concentration of leather fibers, based on the mixture as a whole, is between about 1.5 and about 2.5% by weight.

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If the leather fibers contain chrome-tanned leather or if the leather fibers consist solely of chrome-tanned leather, vegetable tanning agents, for example chestnut wood extract, quebracho, mimosa or valonea, are first added.

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Oiling agents are then added. Suitable oiling agents are any leather oiling agents which are emulsifiable in water. Sulfated fish oils are preferably used, for

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example Licrol® DM 10, a product of Erberle, Coriatol U6, a product of Polychemie, or Coripol 2397, a product of TFL

Dyes may also be added to the mixture. The dyes used are normally
5 quantitatively absorbed iron oxide dyes, for example Bayferrox® 960 (a product of Bayer AG).

Preservatives, for example Preventol A11D (Bayer AG), natural and/or synthetic
fats, natural and/or synthetic oils, silicone oils and/or ionic and/or nonionic surfactants,
10 may also be added to the mixture.

If the additives are insoluble in water or do not self-emulsify in water, they are
generally added to the mixture in the form of emulsions.

15 The polymer dispersion or the mixture of two or more different polymer
dispersions is then added.

If two or more different polymer dispersions are to be used, they may be added
to the mixture either simultaneously or successively in any order.

20 If two polymer dispersions that are differently stabilized, i.e. with different
charges of the stabilizing species, are added to the mixture, the anionically stabilized
polymer dispersion(s) is/are added separately from the cationically stabilized polymer
dispersion(s). The order in which the dispersions are added is of no consequence.

25 After the polymer dispersions have been added, a solution of an aluminum salt
or a copper salt is added to the mixture. Aluminum sulfate is preferably used. About 40
to 300 l, preferably about 100 to about 250 l and, in a particularly preferred
embodiment, about 120 to about 200 l of an approximately 20 to preferably about 60%
30 by weight aluminum sulfate solution are added per 1,000 kg of mixture.

During but preferably after the metal salt treatment, the mixture may be treated
with a solution of a cationically charged polymer. The cationically charged polymer
preferably has a molecular weight of no more than about 150,000 and advantageously
35 in the range from about 80,000 to about 120,000.

The charge density of the cationically charged polymer is about 2.00 to 5.00 meq/g, preferably in the range from about 2.50 to about 4.50 meq/g and more preferably in the range from about 3.00 to about 4.00 meq/g.

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The cationically charged polymer is used in a quantity of about 0.1 to 10% by weight, preferably in a quantity of about 1 to 8% by weight and more preferably in a quantity of about 2 to 6% by weight, based on the total solids in the mixture.

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After stirring for about 1 hour, the mixture is freed from excess water using a suitable drainage machine. Although drainage machines operating on the so-called batch principle, for example a so-called Muller press, may be used for this purpose, continuous drainage in a fourdrinier machine is preferred. The mixture is drained to a residual water content of around 70% by weight in the fourdrinier machine.

15

After the drainage step, the material obtained is pressed in a suitable press, preferably an intermittent press, under a pressure of about 1,000 to about 3,000 t and preferably in the range from about 1,500 to about 2,500 t.

20

The material thus treated is then passed through a suitable thermal dryer, in which it is dried to a residual water content of about 10% by weight, and thereafter is wound onto rolls.

25

The films obtained in this way have a flow transition range of from about 70 to about 130°C and are thus suitable for modern surface coating processes, preferably so-called thermoforming processes.

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An adhesive is generally used to establish a permanent bond between the surface coating material and the surface to be coated. Adhesives in the context of the present invention are understood to be non-metallic, preferably organic materials which bond parts to be joined by surface adhesion and internal strength.

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Suitable adhesives include, for example, glues, dispersion adhesives, solvent-based adhesives and/or contact adhesives.

Organic adhesives - either physically setting adhesives or chemically reacting

adhesives or a combination of the two - are preferably used for the purposes of the invention. Physically setting adhesives which may be used for the purposes of the invention include, for example, dissolved or dispersed adhesives, contact adhesives or hotmelt adhesives. Suitable chemically reacting adhesives are, for example, those
5 which impart adequate adhesion to the surfaces to be joined to one another without emitting volatile constituents. However, it is also possible to use adhesives which produce the necessary adhesion while emitting volatile constituents. The adhesives may be both cold-curing and hot-curing adhesives, may have a thermoplastic, thermoset or elastomeric end state and may be applied as one-component adhesives
10 or as two- or multi-component adhesives.

In general, it is of advantage to expose the surfaces to be joined to a high pressure after they have been fitted together. Accordingly, one particular embodiment of the present invention is characterized by the use of adhesives which, after
15 application of pressure to the surfaces to be joined together, produce improved adhesion in relation to pressureless processing.

The adhesives used in accordance with the present invention advantageously contain at least three different macromolecular compounds as coupling agents.
20

Coupling agents in the context of the present invention are macromolecular compounds which mainly contribute towards the generation of the adhesion and cohesion forces between the surfaces to be bonded.

25 According to the invention, a combination of polyurethane, polyacrylate and ethylene/vinyl acetate copolymer (EVA copolymer), for example, in the form of an aqueous dispersion or hotmelt adhesive is used as the coupling agent.

More particularly, the adhesive according to the invention contains about 30 to
30 120 parts by weight of a preferably anionic polyester polyurethane dispersion.

Polyester polyurethanes can be obtained by reacting generally relatively low molecular weight OH-terminated polyesters with at least difunctional isocyanates to form urethane links. The polyesters generally have a molecular weight of at least about
35 400 and preferably of at least about 500. Both aromatic and aliphatic polyesters may

be used although aromatic polyesters are normally not suitable as the sole polyester component in view of their marked tendency to crystallize and their lack of flexibility.

In general, the acid components involved in the synthesis of the polyester are,
5 for example, aliphatic dicarboxylic acids, such as butane-1,4-dicarboxylic acid, pentane-1,5-dicarboxylic acid, hexane-1,6-dicarboxylic acid, heptane-1,7-dicarboxylic acid and other higher homologs with an increasing number of carbon atoms. In addition, aromatic dicarboxylic acids, for example terephthalic acid or isophthalic acid, may be used.

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In general, any aliphatic dialcohols containing 2 to about 20 carbon atoms may be used as the diol component for the production of the polyesters. Preferred dialcohols are ethylene glycol, propylene glycol, butylene glycol, pentane-1,5-diol, hexane-1,6-diol, heptane-1,7-diol, octane-1,8-diol, nonane-1,9-diol, decane-1,10-diol and higher
15 homologs thereof containing up to 20 carbon atoms. Aliphatic diols containing 2 to 10 carbon atoms and preferably about 4 to 8 carbon atoms are preferably used.

The polyesters may also have been produced using acid or alcohol components with a functionality different from 2. Suitable acid components with a functionality of 3
20 or more are, for example, 1,2,3-propane tricarboxylic acid, hemimellitic acid, trimellitic acid, trimesic acid and 1,2,4,5-benzenetetracarboxylic acid. Trihydric or higher alcohol components are, for example, glycerol, trimethylol propane, pentaerythritol and carbohydrates such as, for example, the monomeric sugar compounds, more especially glucose.

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The reaction products of dihydric or higher alcohols with ethylene oxide and/or propylene oxide may also be used as the diol component.

Basically, mixtures of several different acids and several different alcohols
30 may also be reacted with one another.

The reaction generally proceeds with a stoichiometry which, on the one hand, enables the required molecular weight to be established (generally about 400 to about 10,000 and preferably about 500 to about 5,000) and, at the same time, ensures that
35 the polyester contains at least one hydroxy group in the molecule, preferably as the

terminal group.

The described polyesters are then reacted with isocyanates having a functionality of two or more, for example with triisocyanates or tetra-isocyanates. In principle, any aliphatic or aromatic polyisocyanates may be used for this purpose. Preferred polyisocyanates are, for example, hexamethylene-1,6-diisocyanate, 2,4- and 2,6-toluene diisocyanate and 4,4'-diisocyanatodiphenyl methane (MDI). If toluene diisocyanate is used, it is preferably used in the form of an isomer mixture in which the 2,4- and 2,6-isomers are present in a ratio of about 80 to about 20.

The polyurethanes are preferably present in dispersed form, water preferably being the continuous phase. Anionic emulsifiers are generally used.

In one particularly preferred embodiment, the polyurethane dispersions have a solids content of about 35 to about 65% and a viscosity (according to DIN 53019) of less than about 1,000 mPas, preferably in the range from about 100 to about 900 mPas and more preferably in the range from about 200 to about 800 mPas. The pH value is preferably in the range from about 5 to about 9 and more preferably in the range from about 6.5 to about 7.5. The minimum film forming temperature (DIN 53787) of the preferred polyurethane dispersions is between about 2 and about 10°C, preferably between about 4 and about 6°C and, in a particularly preferred embodiment, around 5°C. The softening point of the films obtainable from these polyurethane dispersions may be above 100°C, as determined in accordance with ASTM D 816, but is preferably of the order of 80°C or lower, for example around 60°C.

Examples of commercially available polyurethane dispersions suitable for use in accordance with the invention are Dispercoll® U 42, Dispercoll® U 53, Dispercoll® U 54, Dispercoll® KA 8481 (products of BAYER AG), Quilastic® DEP-172 and/or Quilastic® 144-66. Dispercoll® U 53 is particularly preferred.

Polyolefins or polyamides are also suitable adhesives and are used in particular as hotmelt adhesives.

The polyacrylates are also preferably used in the form of an aqueous dispersion. In one particularly preferred embodiment, the dispersion is based on

anionic emulsifiers. The polyacrylate dispersions are preferably polymer dispersions which, basically, may already be used as adhesives, so-called acrylate adhesives. Polyacrylates are preferably based on acrylic acid esters, preferably methyl, ethyl, n-butyl, isobutyl or 2-ethylhexyl esters of acrylic acid. The corresponding esters of methacrylic acid may also be used together with or instead of the acrylic acid esters. The acrylates and/or methacrylates may be copolymerized with other substances which contain an olefinically unsaturated double bond. In a preferred embodiment, these other substances are, for example, vinyl esters of carboxylic acids, for example vinyl acetate, or styrene.

The polyacrylates may optionally contain functional groups which allow subsequent crosslinking, for example by an increase in temperature. The functional groups in question are preferably functional groups which can be crosslinked by adding a small quantity of a catalytically active substance and increasing the temperature. In a particularly preferred embodiment, an acid or any other compound which is capable of releasing an acid by an increase in temperature in a suitable environment, for example an aqueous environment, is used as the catalyst. Such compounds as oxalic acid, ammonium chloride, magnesium chloride and/or diammonium phosphate are preferably used.

The polyacrylate dispersions preferably have a viscosity at 23°C (DIN 53019) of about 20 to about 5,000 mPas. The pH value of the preferred dispersions is generally in the range from about 2 to about 9 and preferably in the range from about 2.5 to about 8. All the polyacrylate dispersions used have a minimum film forming temperature (DIN 53787) below about 1°C and preferably below about 0°C. The polyacrylates generally have a glass transition temperature of less than about -20°C, preferably less than -30°C and, in a particularly preferred embodiment, less than -35°C, for example in the range from -40°C to -45°C. The average particle size of the dispersed polyacrylate particles is preferably less than about 70 µm and, more preferably, less than about 65 µm.

Preferred commercial products are obtainable, for example, from BASF under the name of Acronal® V 205, from Merquinsa under the Quiacryl® 126-07 or from Röhm

under the name of Plextol® E 220.

EVA copolymers are copolymers of ethylene and vinyl acetate. The two monomers can be copolymerized in any quantity ratios using radical initiators. The copolymers obtained are characterized by a statistical distribution of the monomer units in the polymer chains. The properties of the EVA copolymers may be varied within wide limits through the molar ratio of ethylene to vinyl acetate. For example, products with an ethylene content of less than 30% by weight are partly crystalline and thermoplastic while products with a vinyl acetate content of about 40 to about 70% by weight are substantially amorphous. The EVA copolymers are generally produced by bulk, emulsion or solution polymerization. The molecular weight of the EVA copolymers used in accordance with the invention is in the range from about 10,000 to about 1,500,000. The EVA copolymers are preferably used in the form of an aqueous dispersion with a solids content of about 40 to about 70% by weight and preferably in the range from about 50 to about 60% by weight. The dispersion has a viscosity (to ISO 2555 at 23°C, Brookfield (RVT), 20 r.p.m., spindle 4) in the range from about 2,000 to about 13,000 mPas. For example, dispersions with a viscosity in the range from about 4,000 to about 6,000 mPas, from about 6,000 to about 12,000 mPas or from about 2,500 to about 4,000 mPas may be used in accordance with the invention. The dispersions have a pH value of about 3 to about 6 and preferably in the range from about 3.8 to about 4.8. The dispersions produce opaque, transparent or clear films and generally have a minimum film forming temperature of less than 5°C, preferably less than about 3°C and, in a particularly preferred embodiment, around 0°C. The films have a tear strength (standard conditioning atmosphere of 23°C/50% relative humidity to DIN 50014) of about 2.5 to about 9 N/mm². For example, dispersions which produce films having a tear strength of about 3 N/mm², 6 N/mm² or about 8 N/mm² may be used in accordance with the invention. The films produced from the dispersions should have an elongation at break (as determined to DIN 50014 in a standard conditioning atmosphere of 23°C/50% relative humidity) of about 500 to about 900%. The films should have a cold crack temperature (DIN 53372) of at most about 4°C.

The adhesive according to the invention may contain other components, for example wetting agents, thickeners, preservatives or defoamers.

Wetting agents are used to improve substrate wetting in aqueous systems. In

the present case, wetting agents improve the wetting of the thermoplastic composite material and of the surface to be bonded thereto. Basically, any surfactants which do not adversely affect the stability of the adhesive dispersion may be used as wetting agents, although polyether-modified dimethyl polysiloxanes are preferably used. The commercially available product BYK® 346, a product of BYK Chemie GmbH, or Lumiten® IRA is particularly suitable.

Organic high molecular weight substances which absorb water and swell in the process, finally changing into viscous solutions, are used as thickeners. Suitable thickeners are, for example, natural thickeners, such as agar agar, carrageen, tragacanth, gum arabic, alginates, pectins, polyoses, guar gum, locust bean gum, starch, dextrans, gelatine or casein. Modified natural materials such as, for example, carboxymethyl cellulose and other cellulose ethers, hydroxyethyl and hydroxypropyl cellulose and gum ethers may also be used.

Organic synthetic thickeners, such as polycarboxylic acids, polyethers, polyimines, polyamides and certain vinyl polymers, are also suitable and are preferably used for the purposes of the present invention. Such thickeners as polyvinyl alcohol or polycarboxylic acids, for example carboxyfunctional acrylate copolymers, or vinyl pyrrolidone copolymers are preferred. The thickeners are used in the form of an aqueous solution or aqueous dispersion with a solids content of generally about 20 to about 40% by weight and preferably in the range from about 25 to about 30% by weight. Commercially available thickeners which may be used for the purposes of the invention are, for example, Collacral® VL (BASF) or Latekoll® D (BASF).

A suitable defoamer is, for example, Agitan® 281 (Munzing Chemie).

A suitable preservative is, for example, Aktizid® RS (Thorchemie).

In another preferred embodiment of the invention, the adhesives mentioned above are used as suitably formulated hotmelt adhesives.

The adhesive is applied to the substrate, preferably a presspahn board, to be coated with the thermoplastic composite material by means of a spray gun or any other suitable tool.

After a drying time of not less than 30 minutes, the sections of the thermoplastic composite material according to the invention are placed onto the substrate to be coated and pressed at a temperature of about 80 to about 100°C. The pressing time is
5 between about 10 and about 240 seconds and preferably between about 30 and about 120 seconds, depending on the thickness of the section. The pressure applied during pressing is in the range from about 2 to about 10 bar and preferably in the range from about 3 to about 6 bar.

10 If the above-mentioned adhesives are used as hotmelt adhesives, the drying time mentioned is no longer necessary. Depending on the open time of the hotmelt adhesives, the sections should be contacted with the substrate and pressed as quickly as possible. The use of hotmelt adhesives is particularly appropriate when extruded materials, for example extruded profiles, are to be coated continuously or
15 discontinuously with the thermoplastic composite material according to the invention.

The present invention also relates to a process for the surface coating of objects with the thermoplastic composite material according to the invention in which the composite material according to the invention and the object are joined by hotmelt
20 adhesive.

The present invention also relates to the use of a thermoplastic composite material according to the invention or a thermoplastic composite material produced in accordance with the invention for the surface coating of objects, more particularly for the
25 profile sheathing of wall, floor and ceiling panels, furniture fronts with or without inner radii, for edge banding or for the surface coating of interiors of motor vehicles, for example dashboards, door mirrors, pillars, garnish moldings, gear levers, parcel shelves, trunk applications and the like.

30 The thermoplastic composite material is preferably applied by thermoforming in a vacuum. The thermoplastic composite material is preferably present in the form of films with a thickness of about 0.5 mm to about 1.0 mm and preferably with a thickness of about 0.6 mm to about 0.8 mm.

35 In another preferred embodiment of the invention, the thermoplastic composite

material according to the invention has a surface coating which may be used, for example, to seal the material. Suitable surface coatings are, for example, thin films of polyurethane, polyester, polyolefins or the like which are laminated onto the surface of the thermoplastic composite material according to the invention using a suitable
5 adhesive.

Accordingly, the present invention also relates to a thermoplastic composite material according to the invention which is laminated on at least one surface with a polymer film, more particularly of polyurethane, polyester or polyolefins.

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In another preferred embodiment of the invention, the film contains dyes or pigments. In another embodiment of the invention, the film has a surface profile, for example in the form of pits or knobs.